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ZnO/carboxymethyl chitosan bionano-composite to impart antibacterial and UV protection for cotton fabric

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ZnO/carboxymethyl chitosan bionano-composite was prepared at different temperatures. ZnO/carboxymethyl chitosan bionano-composite was characterized by UV spectroscopy, FTIR and transmission electron microscope (TEM). The results obtained confirmed the formation of the bionano-composite. The mean sizes of ZnO and carboxymethyl chitosan particles were ≈28 nm and ≈100 nm, respectively. The obtained bionano-composite was used as a finishing agent for cotton fabric to impart UV protection and antibacterial properties (multifunctional finishing) to cotton fabric. The finishing was carried out using pad-dry-cure method. Cotton fabric was characterized by measuring scanning electron microscope (SEM), X-ray diffraction (XRD), UPF ratting and antibacterial properties. Finished cotton fabric exhibits very good antibacterial properties against Gram positive and Gram negative bacteria which increased with increasing the composite concentration and also has a good UV protection which increased with increasing the temperature of curing.

1. Introduction

The application of nanotechnology in the textile area has attracted considerable interest in recent years (Karst & Yang, 2006; Katangur, Patra, & Warner, 2006; Tarimala et al., 2006). Among the metal oxides nanoparticles, titanium dioxide has been widely studied as coating material for textile fabrics to provide functions such as antibacterial activity (Daoud & Xin, 2004), UV protection (Daoud & Xin, 2004; Daoud, Xin, Zhang, & Qi, 2005), and self-cleaning (Bozzi, Yuranova, Guasaquillo, Laub, & Kiwi, 2005; Qi et al., 2006; Yuranova, Mosteo, Bandara, & Laub, 2006). Nano-Ag has been used for imparting antibacterial properties (Qi et al., 2007; Vigneshwaran, Kumar, Kathe, Varadarajan, & Prasad, 2006) ZnO nanoparticles for antibacterial and UV blocking properties (Lee, Yeo, & Jeong, 2003). Metal oxide nanoparticles are more preferable than nano-silver because of cost consideration. In fact ZnO and TiO_2 are non-toxic and chemically stable under exposure to high temperature and are capable of photo-catalytic oxidation (Yadav et al., 2006).

Recently, ZnO has been found highly attractive because of its remarkable application potential in solar cells, sensors, electro-acoustic transducers, photo-diodes and UV light emitting devices, sun-screens, gas sensors, UV absorbers, anti-reflection coatings, photo-catalysis and catalyst (Becheri, Dürr, Nostro, & Baglioni, 2007; Tang, Cheng, Ma, Pang, & Zhao, 2006; Vigneshwaran et al., 2006). ZnO nano-particles have some advantages, compared to silver nano-particle, such as lower cost, white appearance (Vigneshwaran et al., 2006) and UV-blocking property (Becheri et al., 2007). ZnO is also used to reinforce polymeric bionano-composites (Vigneshwaran et al., 2006).

There is a progressive increase in UV radiation on human skin caused by the depletion of the ozone in the earth's atmosphere. As long-term exposure to UV light can result in a series of negative health effects such as acceleration of skin ageing, photodermatosis (acne), erythema (skin reddening), and even severe skin cancer, developing textiles with UV protection functionality has been widely researched so far (Davis, Capjack, Kerr, & Fedosejevs, 1997). Therefore, the target is protecting the wearers from solar UV radiation, the main UV rays that should be blocked by textiles. Many approaches have been investigated to improve the UV protection function of cotton fabrics because cotton textiles are the most regular summer clothes but having the least UV-blocking ability (Dubas, Kumlangdudsana, & Potiyaraj, 2006).

Great interest in the antibacterial finishing of fibres and fabrics for practical applications has been observed (Sun, 2001, chap. 14). Most textile materials currently used in hospitals and hotels are conducive to cross-infection or transmission of diseases caused by micro-organisms. In general, antimicrobial properties can be imparted to textile materials by chemically or physically incorporating functional agents onto fibres or fabrics.

Bionano-composite, a new generation of bionano-composite materials, signify an emerging field in the frontier of materials science, life science, nanotechnology (Drader, Aranda, & Ruiz-Hitzky, 2007). Bionano-composites are composed of a natural polymer

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matrix and organic/inorganic filler with at least one dimension on the nanometer scale. These bionano-composites show the remarkable advantages of biodegradability and biocompatibility in various medical, agricultural, drug release and packaging applications (Mangiacapra, Gorrasi, Sorrentino, & Vittoria, 2006).

Chitosan is a promising polymer matrix for such materials and a powerful chelating agent. In addition to its biodegradability and biocompatibility, this polymer can form various chemical bonds with transition metals and heavy metals components of composite materials and, thus, can enhance the stability of the nano particles. The use of biodegradable polymers is generally limited and by their poor physical and mechanical characteristics by difficulty of processing. This observation refers in full measure to polysaccharides, which are infusible and sparingly soluble polymers; therefore, the design of composite materials on their basis requires new approaches to be advanced.

This paper focuses on the preparation and characterization of ZnO/carboxymethyl chitosan bionano-composite. Application of bionano-composite to textile materials aimed at producing functional textiles by the pad-dry-cure method to impart UV and antibacterial activity to cotton fabric.

2. Experimental

2.1. Materials

Bleached 100% cotton fabric was kindly supplied by Misr Company for spinning and weaving Mehalla El Kobra, Egypt. Chitosan water soluble supplied by Fluka Company. $ZnSO_4\cdot 7H_2O$, NaOH, glacial acetic acid, monochloroacetic acid and isopropyl alcohol are of laboratory grade chemicals.

2.2. Preparation of water soluble carboxymethyl chitosan (N/O-CM-chitosan)

The experimental technique adopted for carboxymethylation of chitosan was as follows: certain volume of sodium hydroxide solution (30%, w/v) was added to 16 g chitosan suspended in isopropyl alcohol. The mixture was left under stirring for 30 min at room temperature. To this mixture, 34 g of monochloroacetic acid was added and the content of the flask was subjected to continuous stirring for 3 h. At the end, the excess alkali was neutralized using glacial acetic acid and the chitosan was precipitated by adding acetone. Finally, the modified chitosan was filtered and washed with isopropyl alcohol/water (70:30) five times and dried at 60 °C. The final product was soluble in water (El-Shafei, Fouda, Knittel, & Schollmeyer, 2008).

2.3. Preparation of ZnO/(N/O-CM-chitosan) bionano-composite

3 g of N/O-CM-chitosan was dissolved in 500 ml of distilled water. The mixture was stirred using magnetic stirrer until complete dissolution of N/O-CM-chitosan. 15 g of $ZnSO_4\cdot 7H_2O$ was added to the solution of N/O-CM-chitosan and stirred vigorously for 15 min. 4 g of NaOH was dissolved in 500 ml of distilled water and added drop wise with constant stirring. The mixture was stirred for 2 h at 25 °C, 50 °C and 90 °C. To obtain ZnO/N/O-CM-chitosan bionano-composite powder, the solution was decanted and finally filtered off. The obtained powder was washed 3 times with distilled water to remove any impurities and finally dried at 80 °C for 3 h to complete the conversion of $Zn(OH)_2$ to ZnO nanoparticles.

2.4. Application of ZnO/(N/O-CM-chitosan) bionano-composite to cotton fabric

Suspensions of different concentrations of the bionano-composite (2–6%) were prepared in distilled water and sonicated for about 15 min. Cotton fabric was immersed in these suspensions and padded to pick up 100%, dried at 100 °C for 5 min and finally cured at 160 °C for 3 min. The cotton fabrics were washed thoroughly with water and dried in open air.

2.5. Characterization

FTIR spectroscopy: FTIR spectroscopy was measured using FT-IR-FT-Raman, model: Nexus 670 (Nicollet-Madison-WI-USA). Cotton fabric was cut into very small pieces; these pieces were mixed with KBr. The spectral range was 400–4000 cm^{-1}.

Scanning electron microscope (SEM), the samples were examined by a JEOL–840X scanning electron microscope, from Japan, magnification range 35–10,000, resolution 200 Å, acceleration voltage 19 kV. All the samples were coated with gold before SEM testing.

Transmission electron microscope (TEM) was measured using Zeiss-EM10-Germany.

X-ray diffraction (XRD): X-ray diffractometer model Philips X' Pert MPP with a type PW 3050/10 goniometer. The diffractometer controlled and operated by a PC computer with the programs P Rofit and used a Mo K(source with wavelength 0.70930 Å, operating with Mo-tube radiation at 50 kV and 40 mA. The scan parameters range from 2° < 2(< 50° with scanning step of 0.03 in the reflection geometry.

UV–vis spectrum: UV–vis spectrum was recorded on Perkin Elmer Lambda 3B UV-Vis spectrometer.

UPF rating and UV transmittance were measured using UV-Shimadzu 3101 PC-Spectrophotometer.

Antibacterial test: for antibacterial experiment, *Staphylococcus aureus* (*S. aureus*, Gram-positive bacteria) and *Escherichia coli* (*E. coli*, Gram-negative bacteria) were used. The antibacterial activity of prepared cotton samples was measured by the inhibition zone method.

3. Results and discussion

3.1. Characterization of carboxymethyl chitosan (N/O-CM-chitosan) by solid state ^{13}C NMR

Carboxymethylation of chitosan is achieved with monochloroacetic acid and sodium hydroxide. According to this reaction takes place preferentially either at C-6 hydroxyl groups or at the NH_2-group resulting in N/O-carboxymethyl chitosan (N/O-CM-chitosan). The solid state ^{13}C NMR spectrum for a typical N-carboxymethyl chitosan shows signals attributed to the N-carboxymethyl substituent, at 47.7 and 168.7 ppm, for N-CH_2 and COOH, respectively, but in case of our results, the solid state ^{13}C NMR described in Fig. 1 shows signals at 73 and 175 ppm which attributed to –O-CH_2– and COOH carboxyl group, respectively. This downfield shift of the carbon indicates the formation of O-carboxymethyl chitosan. The formation of this product agrees with the higher reactivity of hydroxyl group of C6 in this heterogeneous reaction. The N-carboxymethyl substituent is not present because of the absence of peaks at 47 and 168 ppm for N-CH_2 and COOH, respectively.

3.2. Characterization of ZnO/(N/O-CM-chitosan) bionano-composite

ZnO/(N/O-CM-chitosan) bionano-composite was characterized by UV–vis spectroscopy, TEM, XRD and FTIR.

3.2.1. UV spectroscopy

UV–vis spectra of ZnO/(N/O-CM-chitosan) bionano-composite prepared at 25 °C, 50 °C and are shown in Fig. 2. It is clear from Fig. 1

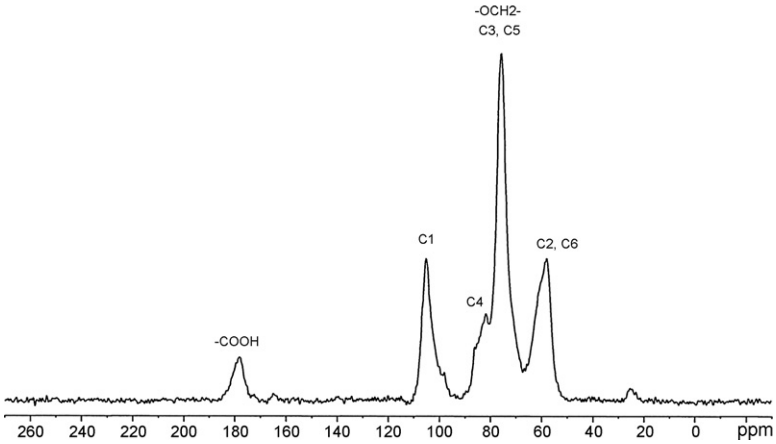

Fig. 1. Solid state ^{13}C NMR spectrum typical for O-carboxymethyl chitosan.

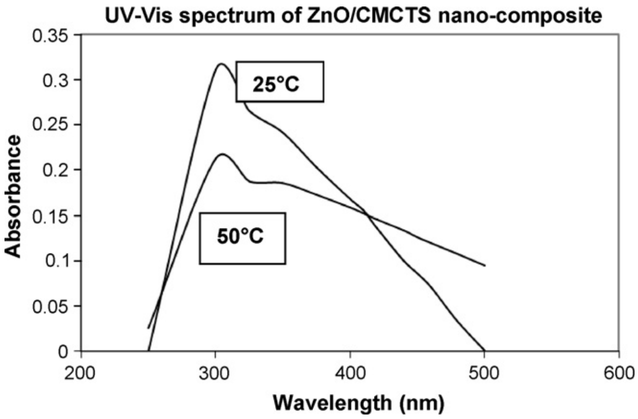

Fig. 2. UV spectroscopy of ZnO/CMCTS bionano-composite.

that the absorption peaks for ZnO/(N/O-CM-chitosan) bionano-composite are 310 nm and 300 nm for the samples prepared at 25 °C and 50 °C, respectively, while the peak of bulk ZnO is at 380 nm which means that by increasing the temperature leads to increasing the concentration of ZnO nanoparticles and decreasing of its particle size. This finding confirms the role of the temperature on the formation of ZnO nanoparticles which facilitate the formation of nanoparticles and prevent its aggregation.

3.2.2. TEM

Fig. 3a and b shows the TEM of ZnO/N/O-CM-CHITOSAN bionano-composite prepared at 50 °C and 25 °C, respectively. It is shown by Fig. 3a and b that ZnO nanoparticles (black dots) prepared at 50 °C seem to be spherical in shape, homogeneous (Fig. 3a) and of particle size smaller than that prepared at 25 °C (the mean particle size is of 28 nm). Also the size of N/O-CM-chitosan particles (white dots) is of about 100 nm in size, and also in spherical and homogeneous in shape. According to the presence of NH_2 and COOH groups in N/O-CM-chitosan, N/O-CM-chitosan seems to act as stabilizer and/or a template of the formation of ZnO nanoparticles, through the formation of coordination bonds with Zn^{2+} (Raveendran, Fu, & Wallen, 2003; Taubert & Wegner, 2002).

3.2.3. FTIR spectroscopy

The composition of ZnO/(N/O-CM-chitosan) bionano-composite was confirmed by FTIR spectroscopy. Fig. 4a and b shows FTIR spectra of N/O-CM-chitosan alone and ZnO/(N/O-CM-chitosan) bionano-composite. As shown in Fig. 4a the absorption peak at about 1400 cm^{-1} and 1600 cm^{-1} are corresponding to carboxyl groups (Rosca, Popa, Lisa, & Chitanu, 2005). And the peak at about 2900 cm^{-1} is attributed to C–H stretching. A broad band at about 3447 cm^{-1} is attributed to OH and NH_2 of chitosan. FTIR spectrum of ZnO/(N/O-CM-chitosan) bionano-composite (Fig. 4b) is similar to that of N/O-CM-chitosan and the band at about 516 cm^{-1} is corresponding to ZnO.

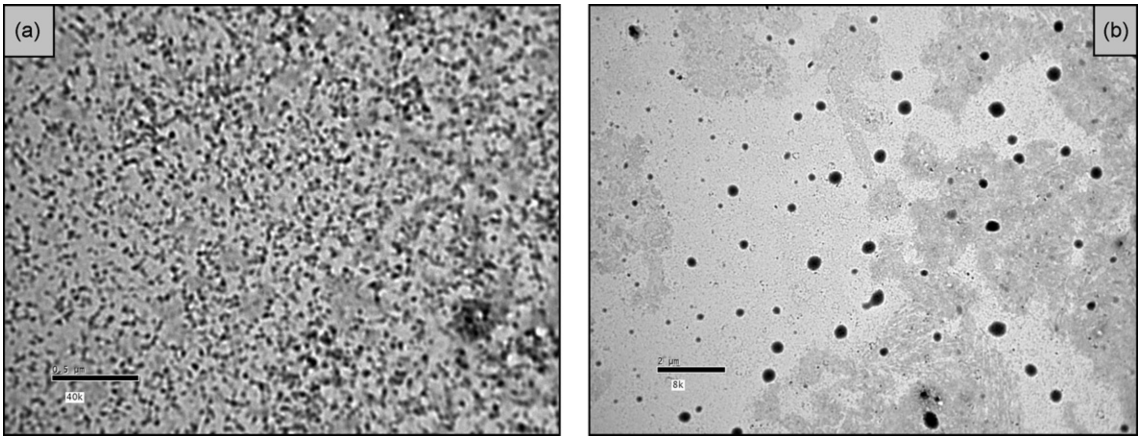

Fig. 3. (a and b) TEM of ZnO/CMCTS bionano-composite prepared at 50 °C and 25 °C, respectively.

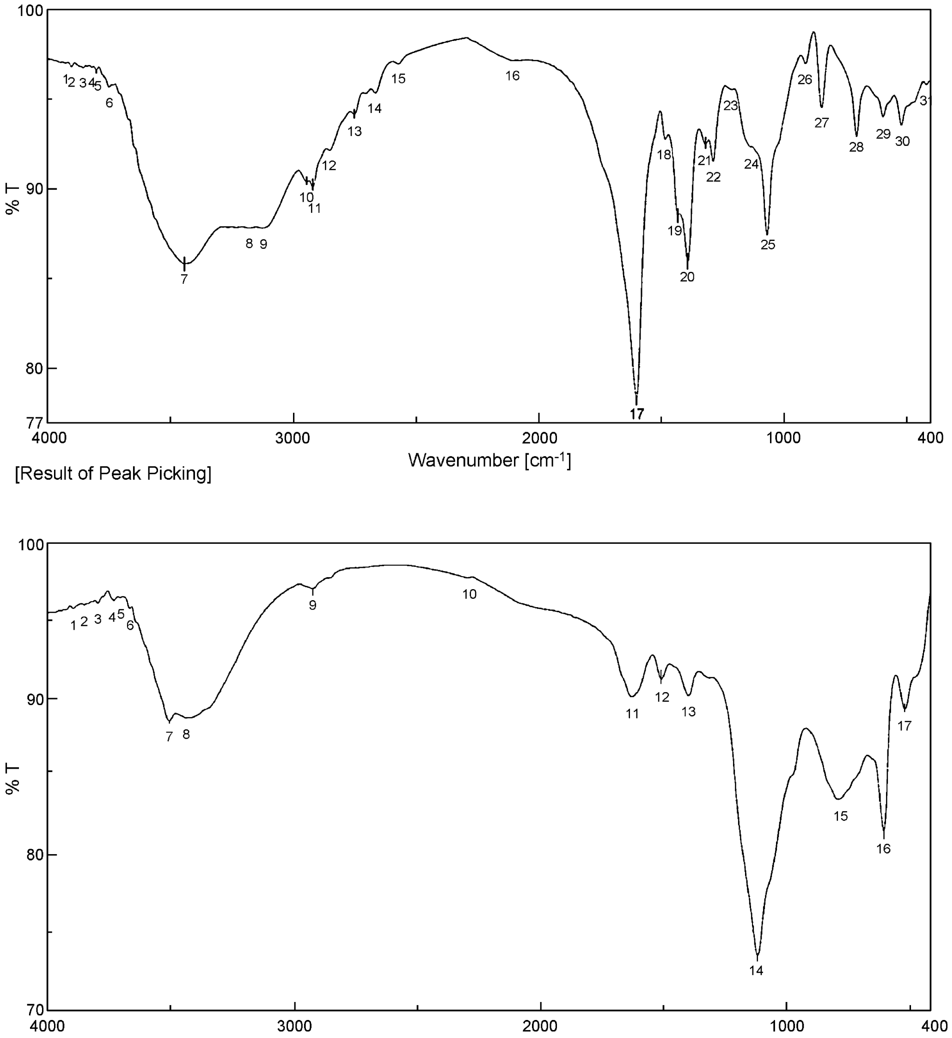

Fig. 4. (a and b) FTIR of carboxymethyl chitosan and ZnO/CMCTS bionano-composite.

3.3. *Characterization of cotton fabric treated with the ZnO/N/O-CM-chitosan bionano-composite*

Cotton fabrics were characterized by measuring antibacterial properties, UPF ratting, UV transmittance. XRD and SEM.

3.3.1. *XRD*

The XRD pattern of cotton fabric treated with 2% ZnO/(N/O-CM-chitosan) bionano-composite is shown in Fig. 5. The characteristic peaks of cotton fabric (Fig. 5) at $2\theta \approx 23^\circ$ which is the intensive peak, and also the less intensive one at $2\theta \approx 14^\circ$ (Swarthmore, 1972). The other bands at 2θ less than 24 are may be attributed to the presence of N/O-CM-chitosan. The broad beak at 2θ from 31° to 36° is related to the ZnO crystallite (Swarthmore, 1988). This broadening is may attributed to the presence of Zn in coordination with NH_2 and COOH groups present in the N/O-CM-chitosan moieties.

3.3.2. *SEM*

SEM was used to characterize the surface of cotton fabric treated with ZnO/(N/O-CM-chitosan) bionano-composite. SEM images of treated cotton fabric and untreated sample are shown in Fig. 6a and b. It is shown that cotton fabric is treated with a uniform and dense film (black) of ZnO nanoparticles (with mean size = 28 nm) (Fig. 6a), while the larger particles (white) are of the larger particles of N/O-CM-chitosan polymer molecules which are of the range 100 nm in size.

3.3.3. *Antibacterial properties*

The antibacterial activity of cotton fabrics was resulted from the presence of ZnO/(N/O-CM-chitosan) bionano-composite on their surface. Antibacterial properties of cotton fabric treated with ZnO/(N/O-CM-chitosan) bionano-composite are measured according to the inhibition zone method against Gram negative bacteria

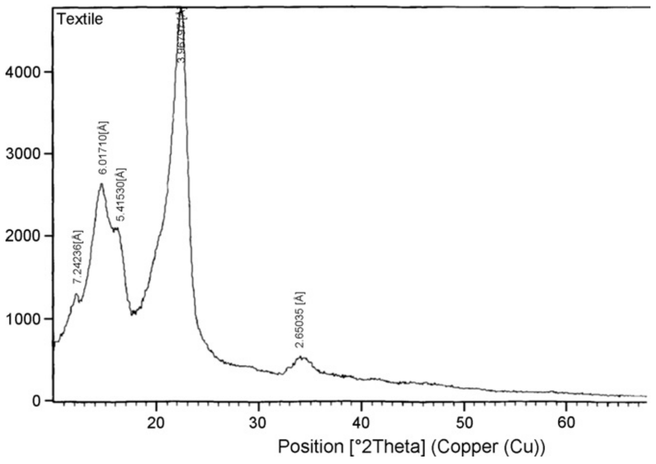

Fig. 5. XRD of cotton fabric treated with ZnO/CMCTS bionano-composite.

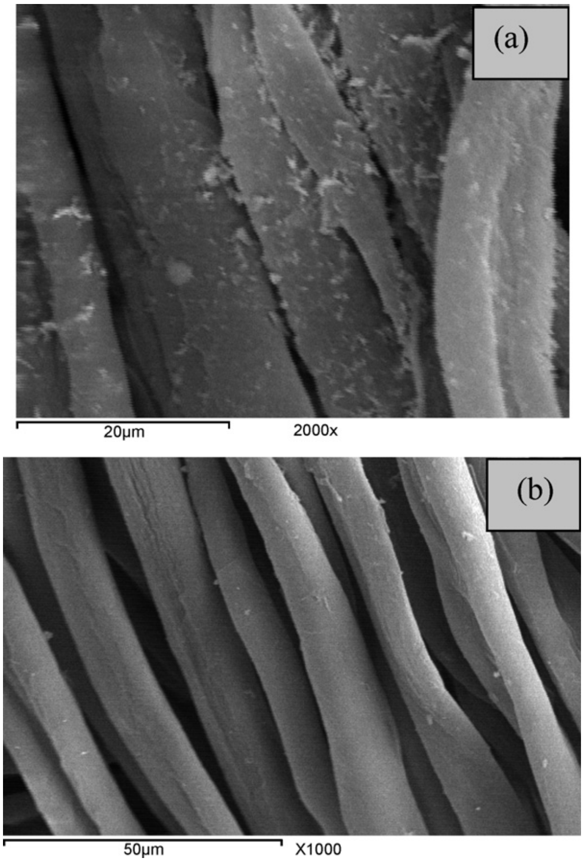

Fig. 6. SEM of cotton fabric and cotton fabric treated with ZnO/CMCTS bionano-composite (a) treated, (b) untreated.

(*E. coli*) and Gram positive one (*S. aureus*). Table 1 shows the results of inhibition zone of treated cotton fabrics with different concentrations of ZnO/N/O-CM-chitosan bionano-composite in the range 2–6%. Table 1 clearly says that all samples have inhibition zone larger than the untreated sample which is obvious from Table 1 and Fig. 6. Also Table 1 shows that the zone increases with increasing the ZnO/(N/O-CM-chitosan) bionano-composite concentration in the range studied (2–6%). Table 1 shows the larger resistivity of the *E. coli* (Gram negative bacteria) compared to the *S. aureus* (Gram positive bacteria) which is related to the differences in the structures of each type.

3.3.4. *UPF and UV transmittance*

Table 2 shows the UPF rating values of the treated cotton fabrics with 2% of the composite at different curing temperatures (120–160 °C). UPF rating values of the treated sample are greater than of the untreated sample. Also UPF values increase with increasing the curing temperature in the range studied as show by Table 2. This finding may be attributed to increasing the concentration of ZnO by conversion of the remained $Zn(OH)_2$ to ZnO under the influence of the higher temperature. UPF values are 5.7, 6.4 and 7.6 at curing temperatures 120 °C, 140 °C and 160 °C, respectively. Also the UV transmittance (in the range 200–400 nm) of the treated sample at different curing temperature decreases with increasing curing temperature which is congruent with the results of UPF and also attributed to the same reason.

Table 1
Inhibition zone diameter of cotton fabric.

Concentration of composite %	Inhibition zone diameter (mm/1 cm sample)	
	Escherichia coli (G^-)	*Staphylococcus aureus* (G^+)
Control	0.0	0.0
2	6	12
4	22	26
6	22	25

Cotton fabric treated with different concentrations of ZnO-CMCTS bionano-composite, 100% pick-up, dried at 100 °C for 5 min cured at 160 °C.

Table 2
UPF ratting of cotton fabric.

Curing temperature	UPF ratting
Control	5
120 °C	5.7
140 °C	6.4
160 °C	7.6

Cotton fabric treated with 2% ZnO-CMCTS bionano-composite, 100% pick-up, dried at 100 °C for 5 min cured at different curing temperatures.

4. Conclusion

In conclusion, a simple method has been developed to prepare nano-ZnO by using ZnO/carboxymethyl chitosan bionano-composite system and coat the same on cotton fabrics to impart functional properties.

The optimum reaction was proceeding at 50 °C results in the formation of smaller nanoparticles with respect to the reaction carried out in water at 25 or 90 °C. In both cases, the nanoparticles appear to be nearly spherical and with a quite narrow size range. The mean sizes of ZnO and carboxymethyl chitosan particles was ≈28 nm and ≈100 nm, respectively. Nanoparticles were analyzed through electron microscopy, X-ray diffraction, FTIR, and specific surface area experiments. The peculiar performance of ZnO nanoparticles as UV-absorbers can be efficiently transferred to fabric materials through the application of ZnO nanoparticles on the surface of cotton fabrics. The UV tests indicate a significant increment of the UV absorbing activity in the ZnO-treated fabrics. Also the treated fabric with indicate significant improve for antibacterial properties for cotton fabric. Such result can be exploited for the protection of the body against solar radiation, bacterial action and for other technological applications.

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